981,715

PATENT SPECIFICATION 981,715

DRAWINGS ATTACHED.

Date of Application and filing Complete Specification: March 18, 1963. No. 10529/63.

Application made in Germany (No. A39883 IVa/6d) on April 5, 1962.

Application made in Switzerland (No. 7553) on June 22, 1962.

Application made in Germany (No. A41693 IVa/6d) on Nov. 23, 1962.

Complete Specification Published: Jan. 27, 1965.

Index at Acceptance:—C6 E(1, 4); B1 D1C2; C1 A13.

Int. Cl.:—C 12 h //B 01 d, C 01 b.

COMPLETE SPECIFICATION.

A Method for the Reduction of Haze in Beer.

We, AKTIENGESELLSCHAFT FUR BRAUEREI-INDUSTRIE GLARUS, of Dufourstrasse 32, Basel, Switzerland, a Swiss Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

The invention relates to a method for the reduction of haze in beer.

Beer contains proteins in colloidal solution, and some of these having a molecular weight of 10,000 to 40,000 tend to coagulate during the storage of the beer, to give an undesirable turbidity or haze. This is sometimes referred to as albumen stability of beer. Beer is treated with an adsorbing agent to remove the haze forming protein substances from the beer and to shorten the storage time of the beer, but leave such types of higher-molecular weight proteins which may be advantageous, such for example as the head-forming substances. The present invention employs a form of silica gel as the selective adsorbing agent and this may be finally separated from the beer by, for example, filtration.

Our Patent No. 938,153 claims a process for the reduction of haze in beer, which comprises admixing with beer a finely powdered silica gel having a surface area of 200—400 $m.^2/g.$, a pore volume of between 0.6 and 1.2 ml./g. and a pore diameter of between 60 and 150 Å, and then filtering off the silica gel from the beer. A feature of that process is that the silica gel may be treated with acid and the acid is then washed out with water until the gel has a *p*H-value of 4.5—7.0 in a 5% suspension in distilled water.

[*Price 4s. 6d.*]

We have now found that the porosity, *p*H and degree of fineness of the silica gel particles are inter-related with regard to the ability of the silica gel to substantially eliminiate any undesired turbidity or haze in beer caused by coagulation or colloidal protein substances during storage of the beer.

The present invention provides in a method for the reduction of haze in beer comprising admixing with beer a finely powdered silica gel being coarse-porous to medium-porous and having a surface area of 200 to 600 $m.^2/g$, a pore volume of 0.5 to 1.5 ml./g. and a pore diameter of 40 to 180 Å, and then filtering off the silica gel from the beer, the step of having ground the silica gel to such a degree as at least 75% by weight passes through a sieve of 44 microns mesh size (325 A.S.T.M. Standard mesh). Preferably the silica gel should show a weakly acid or neutral reaction such that its *p*H value is from 4.0 to 8.0 in a 5% suspension in distilled water.

The inter-relationship of the porosity, *p*H and degree of fineness of the silica gel is such that with optimum coarse-porous particles it is not necessary to employ either the feature of weakly acid to neutral reaction conditions referred to above or grind the silica gel to an optimum degree of fineness provided that at least 75% by weight thereof will pass through a sieve of 44 microns mesh size (325 A.S.T.M. Standard mesh). If, however, the *p*H value of the silica gel is adjusted to an optimum value, provided that it has a *p*H of from 4.0—8.0 in a 5% suspension in distilled water, in addition to coarse-porous silica gels, medium porous silica gels with a normal grind-

ing to increase the albumen stability of beer may also be used.

Where used in this Specification references to a coarse-porous silica gel mean a highly porous product, the surface area of which is relatively small and references to a medium-porous silica gel mean a product which is medium porous, the surface area of which is relatively higher than the surface area of the coarse-porous silica gel. It is realised that these terms are relative but both the coarse-porous and medium-porous silica gel particles should have a surface area of 200 to 600 $m.^2/g.$, a pore volume of 0.5 to 1.5 ml./g. and a pore diameter of 40 to 180 Å. The surface area of the silica gel may be determined by the nitrogen absorption method given in J. Amer. Chem. Soc. 59 (1937) pp. 1553—1564 (Emmett & Brunauer) and 60 (1938), pp. 309—310 (Brunauer, Emmett & Teller) and by Brunauer in "The Absorption of Gases and Vapours", Princeton Univ. Press, 1943; the pore volume may be measured by the methods given in "Kolloid-Zeitschr" 55 (1931), pp. 129—143 (Kubelka) and Ind. Eng. Chem. 17 (1945), pp. 782—791 (Ritter & Drake). The pore diameter is calculated from the pore volume and surface area. If the silica gel is ground to an optimum degree of fineness provided that at least 75% by weight passes through a sieve of 44 microns mesh size (325 A.S.T.M. Standard mesh) coarse-porous and medium porous silica gels may be used in the substantial elimination or reduction of turbidity or haze in beer. Moreover if the silica gel is so ground it is not necessary to maintain a *p*H value of from 4.0 to 8.0 of the silica gel in a 5% suspension in distilled water.

The effect of grinding the silica gel to that extent whereby at least 75% by weight passes through a sieve of 44 microns mesh is surprising, because the surface area and the volume and diameter of the pores of the silica gel are practically unchanged by the degree of the grinding. Thus it may be said that there is no reciprocal action between the particle size of the silica gel and the surface area. (In this connection the degree of fineness of the particle of silica gel according to the present invention is normally greater than that contemplated in our Patent No. 938,153). The reason for this phenomenon resides in the fact that the silica gel is built-up from many fine particles of a substance. The pores of the silica gel are formed by the cavities between these particles and therefore a fine grinding only breaks down the coarse aggregates of the substance into individual particles.

We have now unexpectedly found that extremely finely-ground silica gel is more selectively effective on the turbidity caused by the albumen substances than the less finely-ground material such for example as used in our Patent No. 938,153. The absorption of proteins and pentides is substantially the same for both of these silica gels as shown by the decrease of the nitrogen content of the beer. However the stability of the beer against undesired turbidity or haze formation during the storage is shown by ammonium sulphate precipitation to be substantially increased when the more finely ground silica gel in accordance with this invention is used i.e. at least 75% by weight passes through a sieve of 44 microns mesh size (325 A.S.T.M. Standard mesh). Preferably not less than 90% by weight of the silica gel should pass through the screen of 44 micron mesh size. However as indicated above the porosity, *p*H and degree of fineness of the silica gel may be relatively adjusted whilst still retaining good stability of the beer against undesired turbidity or haze formation during storage. Furthermore we have found that the silica gel not only reduces the haze in the beer but also prevents the decomposition of the micro-organisms therein contained. This advantageous effect of the silica gel is attributed to three causes.

A. The silica gel particles which are suspended in the beer adsorb various micro-organisms. If the beer is agitated during the addition of the silica gel and then the agitation stopped, the silica gel and the adsorbed micro-organisms will gradually settle to the bottom of the containing vessel. The silica gel and adsorbed micro-organisms may be removed by filtration thereby giving a beer which is substantially lower in content of micro-organisms and may even be sterile. Thus the beer may be stored for a considerable time without adversely affecting the palate due to microbiological action.

B. The consolidation of the filter cake depends on the degree of fineness of the silica gel particles during its filtration from the beer. Owing to this restriction of the channels of the filter cake, the micro-organisms are better retained during the filtration. Furthermore because of the adsorbing effect of the silica gel on the micro-organisms as mentioned under A, when filtering a beer containing micro-organisms the filtrate is substantially poorer in micro-organism than if only a filter cake of kieselguhr or cellulose is present.

C. The silica gel also adsorbs from the beer substances upon which yeast and bacteria feed. The nature of the substances are not at present known to us but apparently they vary with the strain of yeast and/or bacteria present. In any event, we have observed that in beer

which has preliminarily been treated with a sufficient amount of silica gel (more than approximately 50 g./ml.) yeast formation is stopped.

If therefore the beer is mixed with a finely ground silica gel having the properties as described above, subsequently filtered to remove the silica gel and carefully racked it need not be mixed with a chemical preserving agent, such as is normally used to prevent undesired turbidity or haze formation during storage, nor pasteurized or sterilized.

In accordance with the invention, the silica gel may be used also to shorten the time of storage for bottom-fermented beer. In this connection, the silica gel is used primarily to allow removal from the beer before storing of non-volatile substances of undesired taste such for example as tannic compounds which have previously had to be removed during storage. Furthermore the silica gel is advantageous in that the time of contact between it and the beer need only be short. The preparation of bottom-fermented beer consists in the following main steps:

(1) Brewing process 6—8 hours;
(2) Main fermentation 6—8 days;
(3) Time of storage 4—10 weeks.

Attempts have been made to rationalise the brewing process. Processes for continuous preparation of the wort have been proposed, the purpose of which is to render the brewing process more economical. Attempts have also been made to perform the main fermentation continuously. It is an object of the present invention to shorten the storage time of the beer to a maximum of 10—14 days or even eliminate it completely because this last main step in the preparation of beer is expensive.

The following discussion relates to the storage of beer.

1. *Final fermentation of the extract:*

During the main fermentation, normally only 60—65% of the extract of the wort is fermented. During subsequent storage fermentation continues until the beer is substantially attenuated. However this final fermentation need not necessarily be effected in the storage cellar; it may be effected during the main fermentation.

2. *Saturation of the beer with carbon dioxide:*

Saturation of the beer with carbon dioxide is effected by carrying out the final fermentation of the beer under counterpressure until the beer is enriched with 5% carbon dioxide or more. This enrichment with carbon dioxide may also be effected by carrying through the main fermentation or at least the final state thereof in closed vessels under counterpressure. A more preferable way consists in recovering the carbon dioxide of the fermentation process and adding to the beer such an amount thereof as is required at any time.

3. *Separation of the yeast:*

The beer still contains a part of the yeast from the main fermentation which settles gradually during the time of storage. If the desired final degree of attenuation is reached during the main fermentation, the presence of yeast during the time of storage is no longer necessary. It may be removed by filtration since separation of the least by natural sedimentation is not normally sufficiently effective.

4. *Clarification of the beer:*

The natural clarification of the beer during the time of storage may have been of importance formerly. Nowadays better clarification is obtained by filtration.

5. *Maturation of flavour:*

Two considerations are involved:— the removal of volatile substances such as hydrogen sulphide and mercaptans and the decomposition of non-volatile substances such as tannic compounds. The removal of the volatile substances such as hydrogen sulphide and mercaptans in conventional brewing operations is effected by washing with carbon dioxide which removes the substances from the beer during the after-fermentation in the storage cellar. Purified carbon dioxide may also be used.

It has now been found that the non-volatile substances, such at tannic compounds, which disturb the flavour of the beer may be removed by treatment of the beer with a silica gel having an adsorbing effect of the type characterised above.

6. *Albumen stabilization of the beer:*

In the second phase of the time of storage, when the individual steps mentioned under 1—5 above have been completed to a considerable degree, the temperature of the beer is lowered to 0° C. and below By this step albumen compounds that are unstable in the cold are precipitated and removed by the subsequent filtration. Other, more effective, means are known to remove these unstable albument compounds, for example, precipitating means, albumen decomposing enzymes or adsorbing agents of which, in West Germany, only the last-mentioned means can be employed due to the purity rules in that country.

From a consideration of the above mentioned individual steps which are effected to the beer during storage, the following way to shorten or eliminate completely the time

of storage without however impairing the quality of beer, is indicated in accordance with this invention.

The beer is brought to the required degree of attenuation in the fermentation vessel by suitably controlling the fermentation. The removal of volatile substances such as hydrogen sulphide and mercaptans is effected by washing with carbon dioxide. A preferred method of washing with carbon dioxide comprises introducing into the beer under counterpressure during the main fermentation a carbon dioxide content higher than that which is finally desired. Release of the excessive carbon dioxide is effected by a reduction in pressure prior to the final filtration of the beer. The gas escaping thereby removes the volatile substances such as hydrogen sulphide and mercaptans. The washing with carbon dioxide may also be carried out in such a manner that an excessively high carbon dioxide content is introduced into the beer after the main fermentation and making the excessive carbon dioxide together with the volatile substances such as hydrogen sulphide and mercaptans escape subsequently by reduction of the counterpressure and, if desired, agitating the beer. In this operation, the carbon dioxide may of course be collected, purified and compressed so that the excess of carbon dioxide employed will not be wasted.

The removal of the yeast is usually effected by filtration after the main fermentation. The non-volatile substances disturbing the flavour of the beer such as tannic compounds are removed, in accordance with the invention, by a treatment with a silica gel having an adsorbing effect. If necessary undesired turbidity or haze formation during storage may be prevented by adding to the beer precipitation agents, for example, tannin, or enzymes or adsorbing agents. As indicated previously this latter stage may be avoided if the beer is mixed with a finely ground silica gel having the properties as described above, subsequently filtered to remove the silica gel and carefully racked.

Following is a description by way of example and with reference to the accompanying drawings of methods of carrying the invention into effect.

EXAMPLE 1. (Figure 1)

In the fermentation vessel A, beer is fermented with bottom yeast until the final degree of fermentation is nearly reached. Thereupon the beer is pumped in the direction of the arrow at first through the filter B where the yeast is filtered off. Then it is passed through the low-temperature cooling device C, where it is cooled down to a temperature of 0° C. or below, and is subsequently carbonized at D to a carbon dioxide content higher than that desired in the end product. The beer is then introduced into the tank E and is allowed to stand until it is racked off; the carbon dioxide content of the beer is gradually lowered to the desired value by reducing the counterpressure. Thus the beer is freed from substantially all the undesired volatile substances such as hydrogen sulphide and mercaptans. Finally, the beer passes through the fine-mesh filter plant G on its way to the racking apparatus. In the present example, this plant is shown as being in the form of a deposit type filter with a metering device F for the filter aid. Moreover, in the present example, in addition to the filter aid, the finely ground silica gel is added also at F, which removes the undesired non-volatile flavour substances mentioned above by adsorption. The silica gel is removed again from the beer at the filter G. If the metered amounts of the silica gel which are added are sufficiently high, the beer flowing from the filter G to the racking station is satisfactory with respect to flavour and also stability to coldness. If lower amounts of silica gel are introduced, an enzyme solution for example may be introduced into the beer simultaneously by the metering device F, thus bringing the stability of the beer to turbidity or haze formation during storage to the desired degree. In addition, this treatment of the beer with silica gel prevents the decomposition of the micro-organisms contained therein.

EXAMPLE 2. (Figure 2)

The closed tank A contains young beer the extract of which has fermented to a considerable degree. This young beer is supersaturated with carbon dioxide, for instance by the employment of a fermentation under pressure or by the introduction of fermenting carbon dioxide. Precipitating additives such as a tannin solution are added to the young beer by means of the metering device B to precipitate albumens and enzymes. thorough mixing and reaction takes place in the tank C. From this tank, the beer passes to the filter D where the colloidal protein substances (which coagulate to cause turbidity of the beer during storage) and yeast are filtered off from the beer. Thereupon, the beer is cooled to a temperature of 0° C. or below at E and thereafter flows into the tank G. Silica gel is added to the beer prior to its entry into the tank G by means of a metering device F. In the tank G, the proper carbon dioxide content is adjusted by lowering the pressure when the excess carbon dioxide together with the volatile substances of disagreeable taste, such as hydrogen sulphide and mercaptans, escape. A substantial amount of silica gel collects in the tank G due to sedimentation. Finally, the beer passes through the fine-mesh filter H to the

racking station. It will be seen that the silica gel in accordance with the invention may be used to substantially eliminate any undesired turbidity or haze formation caused by coagulation of colloidal protein substances during the storage of beer; to prevent or delay the microbiological decay thereof, and to shorter the time of storage of beer and in particular bottom-fermented beer. The silica gel may only allow one of these advantages to be obtained completely at any one time and this is determined by the form of the silica gel and the manner in which it is used. Thus, for example, if the silica gel is used only to eliminate any undesirable turbidity or haze formation caused by coagulation of colloidal protein-substances during storage of the beer, the beer may additionally be pasteurised. If the silica gel is used only to shorten the time of storage of the beer, other means may be used as well to improve the turbidity or haze forming resistance properties of the beer.

WHAT WE CLAIM IS:—

1. In a method for the reduction of haze in beer comprising admixing with beer a finely powdered silica gel being coarse-porous to medium-porous and having a surface area of 200 to 600 $m.^2/g.$, a pore volume of 0.5 to 1.5 ml./g. and a pore diameter of 40 to 180 Å, and then filtering off the silica gel from the beer, the step of having ground the silica gel to such a degree as at least 75% by weight passes through a sieve of 44 microns mesh size (325 A.S.T.M. Standard mesh).

2. A method as claimed in Claim 1 wherein the silica gel has a surface area of 200 to 400 $m.^2/g.$

3. A method as claimed in Claim 1 or Claim 2 wherein the silica gel shows a weakly acid or neutral reaction such that its *p*H-value is 4.0—8.0 in a 5% suspension in distilled water.

4. A method as claimed in Claim 3 wherein the desired *p*H-value is achieved by washing the silica gel with water.

5. A method as claimed in Claim 3 or Claim 4 wherein the silica gel is subjected to a treatment with acid, which acid is thereafter washed out with water so as to secure the desired *p*H-value of the silica gel, whereupon the silica gel is dried.

6. A method as claimed in any one of Claims 1 to 5 wherein a type of silica gel having the desired *p*H is initially used.

7. A method as claimed in any one of Claims 1 to 6 wherein the silica gel is ground to such a degree that at least 90% by weight passes through a screen of 44 microns mesh size (325 A.S.T.M. Standard mesh).

8. A method as claimed in any one of Claims 1 to 7 wherein the beer is brought to the desired final degree of attenuation in the fermentation vessel and the removal of volatile substances is effected by washing the beer with carbon dioxide while the non-volatile substances disturbing the flavour are removed by a treatment with silica gel thereby shortening the time of storage of the beer.

9. A method as claimed in Claim 8 wherein the beer is subjected to a counter-pressure during the main fermentation in the fermenting vessel so as to increase the carbon dioxide content of the beer above that finally desired, whereupon a part of the carbon dioxide is released prior to the final filtration of the beer by reducing the pressure thereby effecting removal of the volatile substances.

10. A method as claimed in Claim 8 wherein the beer is carbonised after the main fermentation in the fermenting vessel to an excessively high carbon dioxide content and thereafter the excessive carbon dioxide is removed to effect removal of the volatile substances.

11. A method as claimed in any one of Claims 8 to 10 wherein the beer is in addition agitated to allow easy evaporation of the excess carbon dioxide.

12. A method as claimed in any one of Claims 8 to 11 wherein the beer is filtered directly after having finished the main fermentation in the fermenting vessel to remove the yeast contained therein.

13. A method as claimed in any one of Claims 8 to 12 wherein tannin or enzymes are added to the beer to precipitate a part of the higher molecular weight protein contained therein.

14. A method as claimed in any one of Claims 1 to 13 wherein there is added to the beer an amount of silica gel which is in excess of the amount necessary for removing the undesired non-volatile substances, in order to additionally reduce haze formation in the beer.

15. A method for the reduction of haze in beer substantially as herein described and with reference to the accompanying drawings.

For the Applicants:—
WILSON, GUNN & ELLIS,
Chartered Patent Agents,
57 Market Street,
Manchester 1.

Abingdon: Printed for Her Majesty's Stationery Office, by Burgess & Son (Abingdon), Ltd.—1965.
Published at The Patent Office, 25 Southampton Buildings, London, W.C.2,
from which copies may be obtained.

981715 COMPLETE SPECIFICATION
1 SHEET This drawing is a reproduction of the Original on a reduced scale

Fig.1

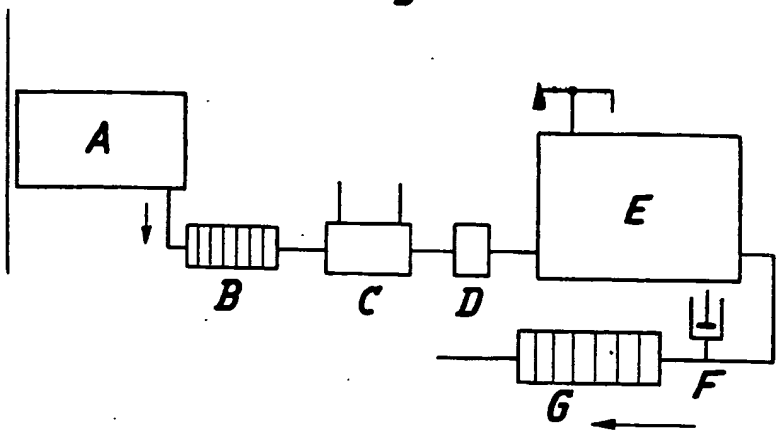

Fig.2